Hydrogenolysis of [PhBP$_3$]Fe≡N-*p*-tolyl: Probing the reactivity of an iron imide with H_2

Steven D. Brown and Jonas C. Peters

Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

Supporting Information

I. Experimental Section

All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. All reagents were purchased from commercial vendors and used without further purification unless otherwise stated. [Li][N(H)-*p*-tolyl] was prepared by reacting *p*-toluidine and n-butyllithium in petroleum ether. The resulting solids were isolated on a sintered glass frit and washed with fresh aliquots of petroleum ether. [$PhBP_3$]FeCl and [$PhBP_3$]Fe≡N-*p*-tolyl (**1**) were prepared according to literature procedures.[1] Elemental analyses were performed by Desert Analytics, Tucson, AZ. Deuterated benzene was purchased from Cambridge Isotope Laboratories, Inc. and was degassed and dried over activated 3 Å molecular sieves prior to use. A Varian Mercury-300 NMR spectrometer was used to record ^{1}H NMR and ^{31}P NMR spectra at ambient temperature. ^{1}H chemical shifts were referenced to residual solvent while ^{31}P chemical shifts were referenced to 85% H_3PO_4 at δ 0 ppm. ^{11}B NMR data was acquired on a Joel 400 MHz spectrometer and chemical shifts were referenced to neat $BF_3{\cdot}OEt_2$ at δ 0 ppm. GC-MS data were obtained by injecting benzene solutions into an Agilent 6890 GC equipped with an Agilent 5973 mass selective detector (EI). ES-MS data for samples were obtained by injecting benzene solutions into a Hewlett-Packard 1100MSD mass spectrometer equipped with an electrospray (ES) ionization chamber. UV-vis measurements were taken on a Hewlett Packard 8452A Diode Array Spectrometer using a quartz cell with a Teflon cap. IR samples were prepared as either a Nujol mull on CaF_2 plates or as a solution in a sealed cell with KBr plates. IR data was collected using a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Bio-Rad Merlin Software (v. 2.97) set at 4 cm^{-1} resolution. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker Smart 1000 CCD diffractometer.

Magnetic Measurements. Measurements were recorded using a Quantum Designs SQUID magnetometer running MPMSR2 software (Magnetic Property Measurement System Revision 2). Data were recorded at 5000 G. Samples were suspended in the magnetometer in a clear plastic straw sealed under nitrogen with Lilly No. 4 gel caps. Loaded samples were centered within the magnetometer using the DC centering scan at 35 K and 5000 G. Data were acquired at 2 – 10 K (one data point every 2 K), 10 – 60 K (one data point every 5 K), and 60 – 250 K (one data point every 10 K). The magnetic susceptibility was adjusted for diamagnetic contributions using the constitutive corrections of Pascal's constants. The molar magnetic susceptibility (χ_m) was calculated by converting the calculated magnetic susceptibility (χ) obtained from the magnetometer to a molar susceptibility (using the multiplication factor {(molecular weight)/[(sample weight)*(field strength)]}). Curie-Weiss behavior was verified by a plot of χ_m^{-1} versus T. Effective magnetic moments were calculated using Equation 1. Solution magnetic moments were measured using Evans method.[2]

$$\mu_{eff} = \mathrm{sqrt}(7.997\ \chi_m T) \quad \text{(eq 1)}$$

[1] Brown, S. D.; Betley, T. A.; Peters, J. C. *J. Am. Chem. Soc.* **2003,** *125,* 322-323.
[2] (a) Sur, S. K. *J. Magn. Reson.* **1989,** *82,* 169. (b) Evans, D. F. *J. Chem. Soc.* **1959,** 2003.

Synthesis of [PhBP$_3$]Fe(N(H)-*p*-tolyl), 2: [PhBP$_3$]FeCl (0.372 g, 0.479 mmol) was added to benzene (10 mL) with stirring. A benzene slurry (2 mL) of [Li][N(H)-*p*-tolyl] (0.0542 g, 0.479 mmol) was then added dropwise at room temperature which resulted in a color change from yellow to opaque red/purple. After stirring for two hours the reaction was filtered over Celite and volatiles were removed under reduced pressure. The crude solids were then washed with petroleum ether (3 x 20 mL) and dried to afford a dark powder. A crude ^{1}H NMR spectrum of the product demonstrated the presence of **2** along with minor paramagnetic impurities. The majority of the impurities were removed by precipitation upon the addition of petroleum ether into a benzene solution. After filtration over Celite the filtrate was chilled to -35 ^{o}C for three days to precipitate 0.194 g (48%) of a dark solid that was predominantly **2** but still contaminated by trace impurities; a crystal suitable for X-ray diffraction analysis was collected from the side of the chilled vial. Subsequent vapor diffusion of petroleum ether into a toluene solution of the nearly pure sample of **2** provided solids of high enough purity to provide satisfactory combustion analysis. Compound **2** was stored at -35 ^{o}C as it degraded over a period of days at room temperature as both a solid and as a benzene solution. ^{1}H NMR (C_6D_6, 300 MHz): δ 139.3 (s); 75.7 (s); 38.3 (s); 18.8 (s); 17.6 (s); 6.63 (s); -11.8 (s); -34.4 (br, s). UV-vis (C_6H_6) λ, nm (ε, M^{-1} cm^{-1}): 450 (3400), 547 (3000). SQUID (solid, average 10 – 250 K): μ_{eff} = 4.92 B.M. IR (Nujol): 3326 cm^{-1} (w). Anal. Calcd. for $C_{52}H_{49}BFeNP_3$: C, 73.69; H, 5.83; N, 1.65. Found: C, 73.29; H, 5.71; N, 1.60.

Synthesis of [PhBP$_3$]Fe(η^5-cyclohexadienyl), 3: [PhBP$_3$]FeCl (0.050 g, 0.0644 mmol) was added to benzene (3 mL) with stirring. A benzene solution (1 mL) of [K][HBEt$_3$] (71 μL of a 1.0 M solution in THF, 0.0708 mmol) was then added dropwise. After stirring overnight the reaction was filtered over Celite and volatiles were removed under reduced pressure. The resulting solids were washed with petroleum ether (1 x 5 mL) and dried under reduced pressure to yield **3** as an orange powder (0.036 g, 68%). X-ray quality crystals may be obtained by vapor diffusion of petroleum ether into a THF solution. ^{1}H NMR (C_6D_6, 300 MHz): δ 8.01 (d, *J* = 7.0 Hz, 2H); 7.55 (t, *J* = 7.5 Hz, 2H); 7.34 (t, *J* = 7.5 Hz, 1H); 7.07 (br s, 12H), 6.94 (t, *J* = 7.5 Hz, 6H); 6.77 (t, *J* = 7.5 Hz, 12H); 5.98 (t, *J* = 4.5 Hz, 1H); 5.16 (t, *J* = 4.5 Hz, 2H); 2.66 (m, 2H); 2.29 (m, 2H); 1.65 (br s, 6H). ^{31}P{^{1}H} NMR (C_6D_6, 121.4 MHz): δ 52.0 ppm (s). ES-MS: calcd. for $C_{51}H_{48}BFeP_3$ [M]$^+$ 821 m/z, found [M]$^+$ 821 m/z. Anal. Calcd. for $C_{51}H_{48}BFeP_3$: C, 74.65; H, 5.90. Found: C, 74.32; H, 6.00.

Synthesis of [PhBP$_3$]Fe(HBEt$_3$), 4: [PhBP$_3$]FeCl (0.100 g, 0.129 mmol) was added to Et_2O (10 mL) with stirring. To the stirring slurry of [PhBP$_3$]FeCl, an ethereal solution (2 mL) of [K][HBEt$_3$] (129 μL of a 1 M solution in THF, 0.129 mmol) was added dropwise over a period of 5 minutes. By the time the addition was complete the reaction was midnight blue in color and precipitates were evident. After stirring at room temperature for 20 minutes, the crude reaction was filtered over Celite and the filtrate was cooled to -35 ^{o}C overnight. Approximately 0.060 g (55%) of midnight blue solid was isolated and dried under reduced pressure. We have thus far been unsuccessful in our attempts to obtain crystals suitable for an X-ray diffraction experiment or a sample of sufficient purity to yield a satisfactory combustion analysis. ^{1}H NMR (THF-d_8, 300 MHz): δ 7.61 (d, *J* = 7.2 Hz, 2H); 7.27 (br s, 12H); 7.15 (t, *J* = 7.2 Hz, 6H); 7.02 (m, 14H); 6.88 (t, *J* = 7.2 Hz, 1H); 1.44 (br d, *J* = 10.8 Hz, 6H); 0.91 (br s, 6H); 0.68 (t, *J* = 6.6 Hz, 9H). The hydride resonance was not located in the ^{1}H NMR spectrum. ^{31}P{^{1}H} NMR (THF-d_8, 121.4

MHz): δ 55.0 ppm (br s). $^{11}B\{^1H\}$ NMR (THF-d_8, 128.3 MHz): δ 25.5 ppm (br s, H*B*Et$_3$); -12.8 ppm (s, Ph*B*(CH$_2$PPh$_2$)$_3^-$). IR (KBr/THF): ν_{BH} = 2448 cm^{-1} (br m).

Reaction of [PhBP$_3$]Fe≡N-*p*-tolyl with H$_2$: [PhBP$_3$]Fe≡N-*p*-tolyl (0.506 g, 0.598 mmol) was dissolved in benzene (30 mL) and loaded into a 250 mL sealable flask equipped with a stir bar. The flask was evacuated, flushed with 1 atm of H_2, and sealed with a Teflon stopcock. After stirring at room temperature for 3 days, volatiles were removed under reduced pressure and the resulting solids were stirred in Et_2O (20 mL) for 3 hours. The ethereal suspension was filtered over a sintered glass frit and [PhBP$_3$]Fe(η^5-cyclohexadienyl) (**3**) was isolated as an orange solid (0.121 g, 25%) from which X-ray quality crystals were grown via vapor diffusion of petroleum ether into a THF solution. The filtrate was collected and the volatiles were removed under reduced pressure. The resulting dark solids were washed with petroleum ether (3 x 20 mL) and dried to yield 0.205 g of **2** which was slightly contaminated with paramagnetic impurities (^{1}H NMR spectroscopy). NMR integration of this isolated sample versus an internal ferrocene standard demonstrated that **2** had been produced in 60% yield from **1** after 3 days.

When the hydrogenation reaction was carried out in C_6D_6, the cyclohexadienyl resonances at δ 5.98, 5.16, and 2.29 ppm disappeared, while the multiplet at δ 2.66 ppm collapsed into a singlet. In C_6D_6 with D_2, the singlet at δ 2.66 ppm disappeared.

Reaction of [PhBP$_3$]Fe≡N-*p*-tolyl with D$_2$: [PhBP$_3$]Fe≡N-*p*-tolyl (0.0114 g, 0.0135 mmol) was dissolved in benzene-d_6 and loaded into a sealable NMR tube. The NMR tube was then evacuated and flushed with 1 atm of D_2. After 3 days NMR integration against an internal ferrocene reference demonstrated the following product yields: [PhBP$_3$]Fe(N(D)-*p*-tolyl), 10%; [PhBP$_3$]Fe(η^5-cyclohexadienyl-d_7), 5%; D_2N-*p*-tolyl, 33%. Additionally, no ^{1}H NMR ring resonances were observed for the η^5-cyclohexadienyl-d_7 moiety of [PhBP$_3$]Fe(η^5-cyclohexadienyl-d_7). Volatiles were then removed under reduced pressure and IR analysis confirmed a weak vibration at 2462 cm^{-1} (Nujol) for **2**. ES-MS of the crude solids verified an [M]$^+$ ion at 828 m/z for [PhBP$_3$]Fe(η^5-cyclohexadienyl-d_7) while GC-MS demonstrated that the only p-toluidine in solution was D_2N-*p*-tolyl with a base peak 2 mass units greater than that for H_2N-*p*-tolyl.

Reaction of [PhBP$_3$]Fe≡N-*p*-tolyl with H$_2$ in CD$_2$Cl$_2$: [PhBP$_3$]Fe≡N-*p*-tolyl (0.0098 g, 0.012 mmol) was dissolved in CD_2Cl_2 and loaded into a sealable NMR tube. The NMR tube was then evacuated and flushed with 1 atm of H_2. After 3 days, NMR integration against an internal ferrocene reference demonstrated the following product yields: [PhBP$_3$]Fe(N(H)-*p*-tolyl), 0%; [PhBP$_3$]FeCl, 30%; H_2N-*p*-tolyl, 80%. Unidentified diamagnetic as well as paramagnetic species were also present in the reaction matrix.

Reaction of [PhBP$_3$]Fe(N(H)-*p*-tolyl) with H$_2$ in C$_6$D$_6$: [PhBP$_3$]Fe(N(H)-*p*-tolyl) (0.0083 g, 0.0098 mmol) was dissolved in C_6D_6 and loaded into a sealable NMR tube. The NMR tube was then evacuated and flushed with 1 atm of H_2. After 3 days, NMR integration against an internal ferrocene reference demonstrated the following product yields: [PhBP$_3$]Fe(η^5-cyclohexadienyl-d_6) 30%; H_2N-*p*-tolyl, 50%. Unidentified paramagnetic species were also present in the reaction matrix.

Kinetic Analysis for the Consumption of [PhBP$_3$]Fe≡N-*p*-tolyl: Equal volumes of 0.018 M solutions of **1** were exposed to 1 atm of either H_2 or D_2 in a sealable NMR tube containing an internal ferrocene standard. The decay of **1** was then monitored by ^{1}H NMR spectroscopy for a minimum of 4 half lives (Figure 1). Analysis of this data revealed a kinetic isotope effect (k_H/k_D) of 5.6, with rate constants of k(H) = 3.85 x 10^{-4} s^{-1} and k(D) = 6.88 x 10^{-5} s^{-1}**.**

Figure 1. Kinetic data for the consumption of [PhBP$_3$]Fe≡N-*p*-tolyl with H_2 and D_2 in C_6D_6.

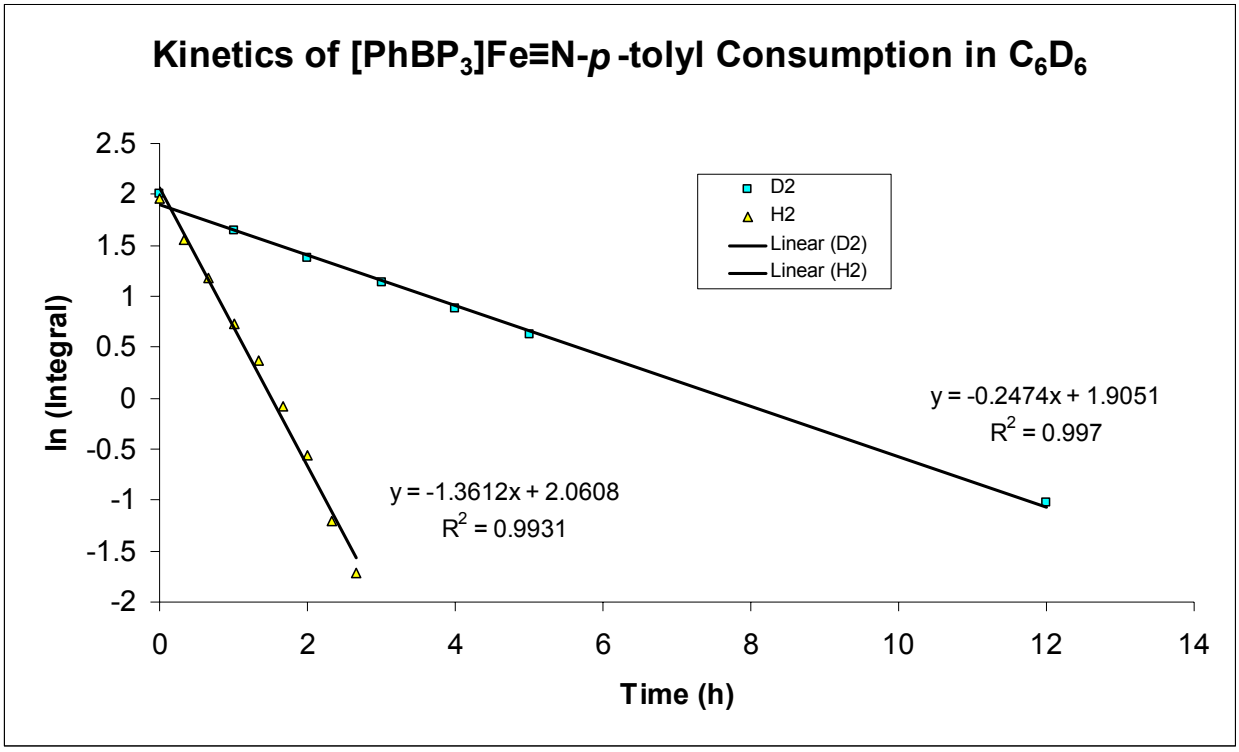

Figure 2. Core labeled drawing of [$PhBP_3$]Fe(N(H)-*p*-tolyl). Hydrogen atoms have been omitted for clarity.

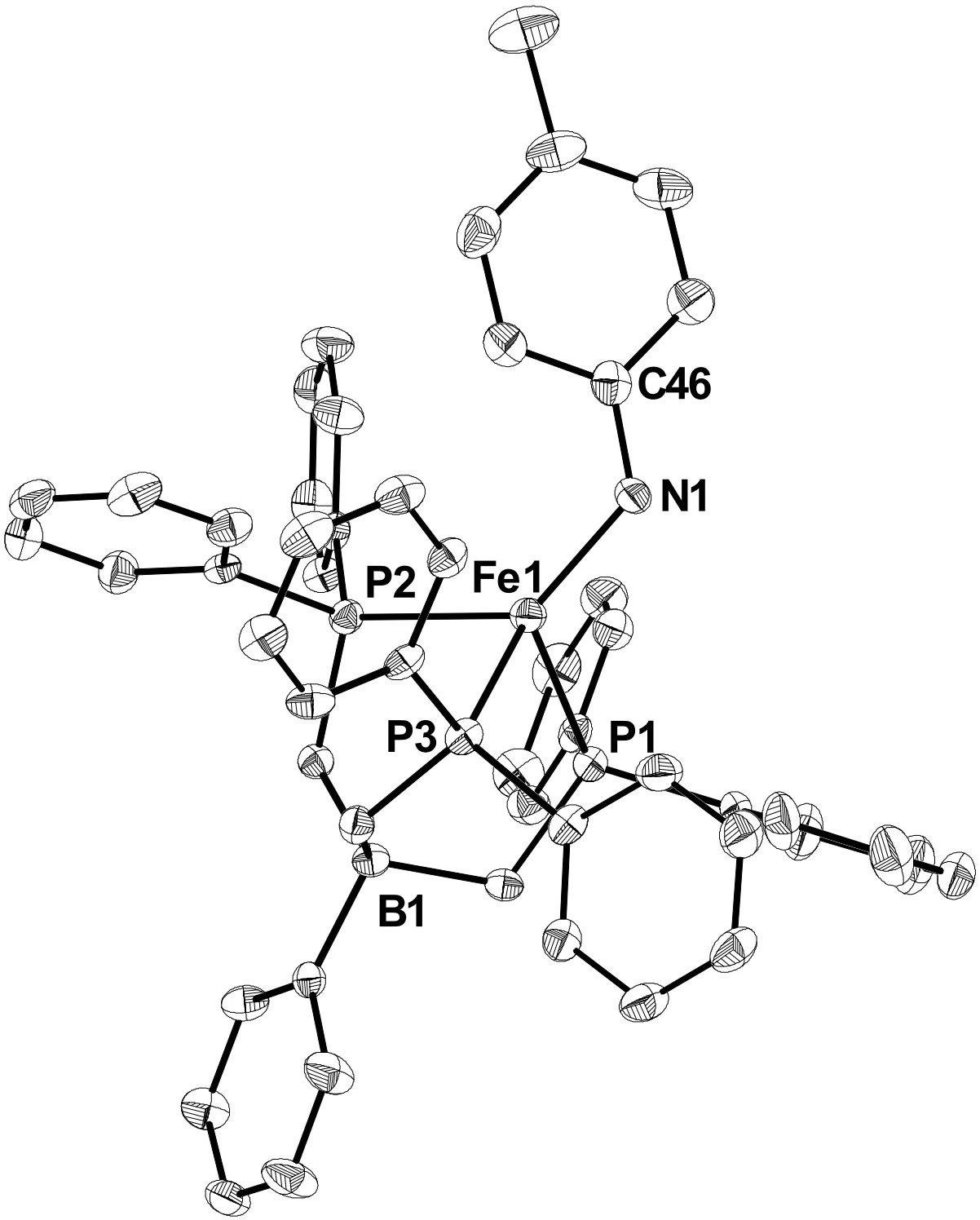

Figure 3. Core labeled drawing of $[PhBP_3]Fe(\eta^5$-cyclohexadienyl). Hydrogen atoms have been omitted for clarity.

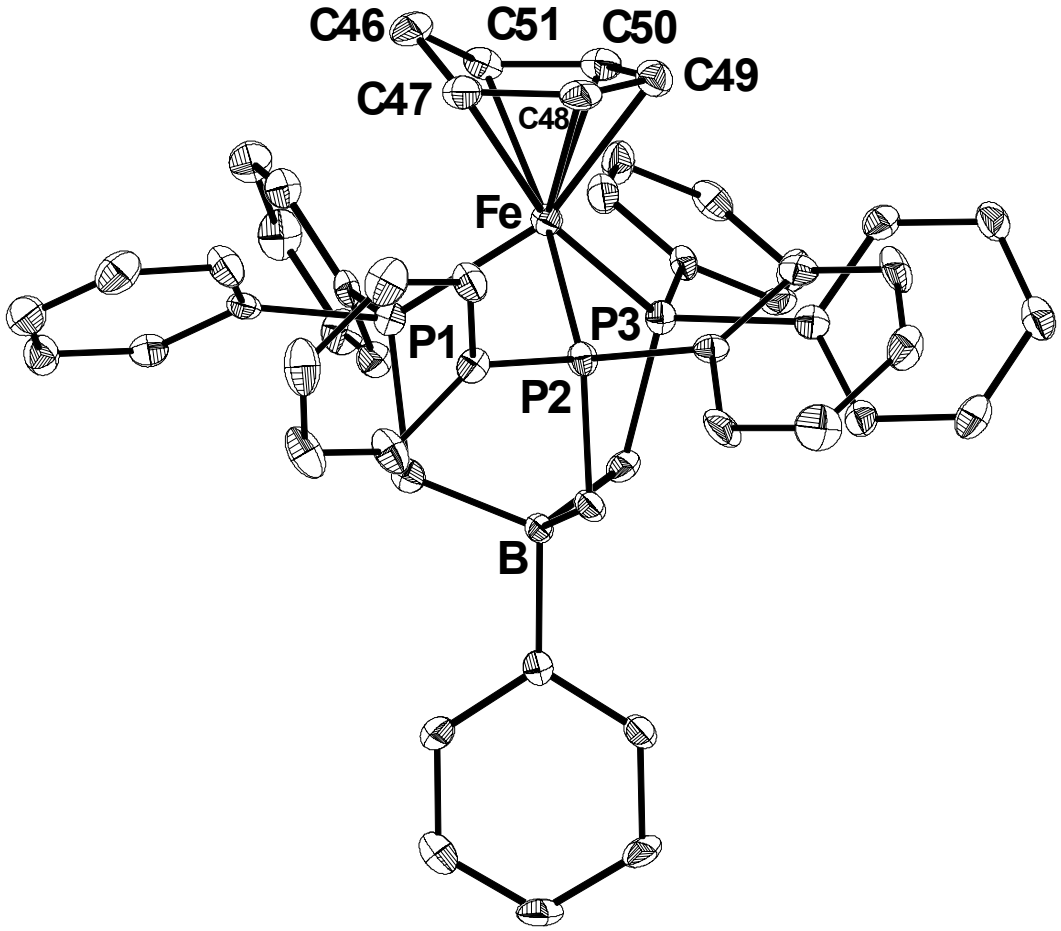

Table 1. Crystal data and structure refinement for [$PhBP_3$]Fe(N(H)-*p*-tolyl) (**2**).

Identification code	sdb38	
Empirical formula	C_{52} H_{49} B Fe N P_3	
Formula weight	847.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.0087(9) Å	α= 80.110(2)°.
	b = 14.8340(13) Å	β= 77.925(2)°.
	c = 15.2850(13) Å	γ = 87.176(2)°.
Volume	2186.0(3) $Å^3$	
Z	2	
Density (calculated)	1.288 Mg/m^3	
Absorption coefficient	0.492 mm^{-1}	
F(000)	888	
Crystal size	0.21 x 0.21 x 0.41 mm^3	
Theta range for data collection	1.79 to 28.36°.	
Index ranges	-13<=h<=12, -19<=k<=19, -20<=l<=20	
Reflections collected	38891	
Independent reflections	10010 [R(int) = 0.0567]	
Completeness to theta = 28.36°	91.5 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10010 / 0 / 524	
Goodness-of-fit on F^2	1.956	
Final R indices [I>2sigma(I)]	R1 = 0.0489, wR2 = 0.0813	
R indices (all data)	R1 = 0.0776, wR2 = 0.0846	
Largest diff. peak and hole	1.121 and -0.483 e.$Å^{-3}$	

Special Refinement Details

SADABS was applied to the hkl file before refinement proceeded. Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [$PhBP_3$]Fe(N(H)-*p*-tolyl) (**2**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe(1)	4096(1)	2200(1)	2993(1)	20(1)
N(1)	2667(2)	1839(1)	4025(1)	26(1)
P(1)	5794(1)	1038(1)	2698(1)	19(1)
P(2)	5889(1)	3333(1)	2777(1)	18(1)
P(3)	3838(1)	2591(1)	1428(1)	20(1)
B(1)	6890(3)	2482(2)	1123(2)	18(1)
C(1)	8180(2)	2510(2)	260(1)	18(1)
C(2)	8040(3)	2215(2)	-541(2)	33(1)
C(3)	9127(3)	2121(2)	-1239(2)	40(1)
C(4)	10436(2)	2317(2)	-1182(2)	28(1)
C(5)	10617(2)	2618(2)	-413(2)	27(1)
C(6)	9512(2)	2712(2)	283(2)	23(1)
C(7)	6685(2)	1360(2)	1524(1)	19(1)
C(8)	7295(2)	3027(2)	1900(1)	18(1)
C(9)	5503(2)	2973(2)	768(1)	21(1)
C(10)	5243(2)	-142(2)	2829(2)	23(1)
C(11)	4121(3)	-295(2)	2480(2)	38(1)
C(12)	3655(3)	-1180(2)	2554(2)	49(1)
C(13)	4299(4)	-1903(2)	2993(2)	49(1)
C(14)	5411(3)	-1766(2)	3341(2)	52(1)
C(15)	5885(3)	-887(2)	3255(2)	41(1)
C(16)	7031(2)	942(2)	3434(1)	19(1)
C(17)	6508(3)	920(2)	4358(2)	26(1)
C(18)	7366(3)	855(2)	4964(2)	32(1)
C(19)	8766(3)	820(2)	4661(2)	33(1)
C(20)	9309(3)	840(2)	3745(2)	33(1)
C(21)	8434(2)	896(2)	3137(2)	25(1)
C(22)	5517(2)	4543(2)	2396(1)	18(1)
C(23)	6533(3)	5187(2)	2244(2)	27(1)
C(24)	6280(3)	6101(2)	1945(2)	34(1)
C(25)	5002(3)	6379(2)	1785(2)	33(1)

C(26)	3981(3)	5756(2)	1938(2)	32(1)
C(27)	4236(2)	4841(2)	2253(2)	26(1)
C(28)	6554(2)	3427(2)	3785(1)	19(1)
C(29)	7872(2)	3162(2)	3891(2)	23(1)
C(30)	8315(3)	3271(2)	4671(2)	27(1)
C(31)	7452(3)	3647(2)	5344(2)	29(1)
C(32)	6141(3)	3899(2)	5255(2)	32(1)
C(33)	5695(3)	3790(2)	4483(2)	28(1)
C(34)	2595(2)	3506(2)	1253(2)	20(1)
C(35)	2785(2)	4182(2)	472(2)	26(1)
C(36)	1851(3)	4901(2)	405(2)	30(1)
C(37)	734(3)	4958(2)	1091(2)	32(1)
C(38)	531(2)	4292(2)	1861(2)	29(1)
C(39)	1450(2)	3572(2)	1940(2)	23(1)
C(40)	3234(2)	1694(2)	924(2)	20(1)
C(41)	1975(2)	1297(2)	1343(2)	29(1)
C(42)	1467(3)	614(2)	996(2)	33(1)
C(43)	2199(3)	319(2)	225(2)	32(1)
C(44)	3445(3)	703(2)	-196(2)	31(1)
C(45)	3959(2)	1385(2)	155(2)	25(1)
C(46)	2071(2)	2349(2)	4671(2)	24(1)
C(47)	1404(2)	1968(2)	5553(2)	31(1)
C(48)	847(3)	2520(2)	6186(2)	37(1)
C(49)	912(3)	3471(2)	5985(2)	36(1)
C(50)	1555(3)	3842(2)	5113(2)	36(1)
C(51)	2106(3)	3302(2)	4473(2)	33(1)
C(52)	329(3)	4082(2)	6668(2)	51(1)

Table 3. Bond lengths [Å] and angles [°] for [$PhBP_3$]Fe(N(H)-*p*-tolyl) (**2**).

Fe(1)-N(1)	1.9132(18)	C(19)-C(20)	1.388(3)
Fe(1)-P(1)	2.3928(7)	C(20)-C(21)	1.394(3)
Fe(1)-P(3)	2.4267(7)	C(22)-C(27)	1.384(3)
Fe(1)-P(2)	2.4520(7)	C(22)-C(23)	1.386(3)
N(1)-C(46)	1.367(3)	C(23)-C(24)	1.384(3)
P(1)-C(7)	1.822(2)	C(24)-C(25)	1.382(3)
P(1)-C(10)	1.826(2)	C(25)-C(26)	1.368(3)
P(1)-C(16)	1.826(2)	C(26)-C(27)	1.389(3)
P(2)-C(8)	1.828(2)	C(28)-C(33)	1.391(3)
P(2)-C(28)	1.829(2)	C(28)-C(29)	1.392(3)
P(2)-C(22)	1.834(2)	C(29)-C(30)	1.393(3)
P(3)-C(9)	1.819(2)	C(30)-C(31)	1.374(3)
P(3)-C(34)	1.819(2)	C(31)-C(32)	1.375(3)
P(3)-C(40)	1.832(2)	C(32)-C(33)	1.382(3)
B(1)-C(1)	1.638(3)	C(34)-C(39)	1.396(3)
B(1)-C(8)	1.670(3)	C(34)-C(35)	1.407(3)
B(1)-C(7)	1.679(3)	C(35)-C(36)	1.387(3)
B(1)-C(9)	1.683(3)	C(36)-C(37)	1.373(3)
C(1)-C(6)	1.390(3)	C(37)-C(38)	1.387(3)
C(1)-C(2)	1.403(3)	C(38)-C(39)	1.381(3)
C(2)-C(3)	1.376(3)	C(40)-C(45)	1.383(3)
C(3)-C(4)	1.379(3)	C(40)-C(41)	1.397(3)
C(4)-C(5)	1.374(3)	C(41)-C(42)	1.384(3)
C(5)-C(6)	1.385(3)	C(42)-C(43)	1.379(3)
C(10)-C(11)	1.384(3)	C(43)-C(44)	1.379(3)
C(10)-C(15)	1.385(3)	C(44)-C(45)	1.389(3)
C(11)-C(12)	1.393(4)	C(46)-C(51)	1.395(3)
C(12)-C(13)	1.372(4)	C(46)-C(47)	1.407(3)
C(13)-C(14)	1.367(4)	C(47)-C(48)	1.385(3)
C(14)-C(15)	1.384(4)	C(48)-C(49)	1.393(4)
C(16)-C(21)	1.385(3)	C(49)-C(50)	1.385(3)
C(16)-C(17)	1.395(3)	C(49)-C(52)	1.507(3)
C(17)-C(18)	1.378(3)	C(50)-C(51)	1.379(3)
C(18)-C(19)	1.382(3)		

N(1)-Fe(1)-P(1)	114.15(6)	C(5)-C(4)-C(3)	118.1(2)
N(1)-Fe(1)-P(3)	126.19(6)	C(4)-C(5)-C(6)	120.5(2)
P(1)-Fe(1)-P(3)	94.44(2)	C(5)-C(6)-C(1)	123.3(2)
N(1)-Fe(1)-P(2)	129.34(6)	B(1)-C(7)-P(1)	117.24(15)
P(1)-Fe(1)-P(2)	90.29(2)	B(1)-C(8)-P(2)	117.00(15)
P(3)-Fe(1)-P(2)	92.64(2)	B(1)-C(9)-P(3)	117.35(15)
C(46)-N(1)-Fe(1)	127.44(16)	C(11)-C(10)-C(15)	118.4(2)
C(7)-P(1)-C(10)	107.08(10)	C(11)-C(10)-P(1)	117.85(19)
C(7)-P(1)-C(16)	108.96(10)	C(15)-C(10)-P(1)	123.7(2)
C(10)-P(1)-C(16)	102.70(11)	C(10)-C(11)-C(12)	120.6(3)
C(7)-P(1)-Fe(1)	106.50(8)	C(13)-C(12)-C(11)	119.6(3)
C(10)-P(1)-Fe(1)	118.56(8)	C(14)-C(13)-C(12)	120.7(3)
C(16)-P(1)-Fe(1)	112.69(8)	C(13)-C(14)-C(15)	119.7(3)
C(8)-P(2)-C(28)	108.91(10)	C(10)-C(15)-C(14)	121.0(3)
C(8)-P(2)-C(22)	104.81(10)	C(21)-C(16)-C(17)	118.6(2)
C(28)-P(2)-C(22)	99.98(10)	C(21)-C(16)-P(1)	124.54(17)
C(8)-P(2)-Fe(1)	107.10(7)	C(17)-C(16)-P(1)	116.83(18)
C(28)-P(2)-Fe(1)	115.87(7)	C(18)-C(17)-C(16)	120.9(2)
C(22)-P(2)-Fe(1)	119.36(8)	C(17)-C(18)-C(19)	120.2(2)
C(9)-P(3)-C(34)	108.45(11)	C(18)-C(19)-C(20)	119.9(2)
C(9)-P(3)-C(40)	109.22(11)	C(19)-C(20)-C(21)	119.5(2)
C(34)-P(3)-C(40)	101.93(10)	C(16)-C(21)-C(20)	120.8(2)
C(9)-P(3)-Fe(1)	106.32(7)	C(27)-C(22)-C(23)	118.2(2)
C(34)-P(3)-Fe(1)	113.33(7)	C(27)-C(22)-P(2)	121.83(18)
C(40)-P(3)-Fe(1)	117.34(8)	C(23)-C(22)-P(2)	119.98(18)
C(1)-B(1)-C(8)	109.73(18)	C(24)-C(23)-C(22)	120.9(2)
C(1)-B(1)-C(7)	103.58(18)	C(25)-C(24)-C(23)	119.8(2)
C(8)-B(1)-C(7)	110.83(17)	C(26)-C(25)-C(24)	120.2(2)
C(1)-B(1)-C(9)	109.83(17)	C(25)-C(26)-C(27)	119.7(2)
C(8)-B(1)-C(9)	110.27(18)	C(22)-C(27)-C(26)	121.2(2)
C(7)-B(1)-C(9)	112.40(19)	C(33)-C(28)-C(29)	118.2(2)
C(6)-C(1)-C(2)	114.2(2)	C(33)-C(28)-P(2)	118.05(17)
C(6)-C(1)-B(1)	124.28(19)	C(29)-C(28)-P(2)	123.77(17)
C(2)-C(1)-B(1)	121.0(2)	C(28)-C(29)-C(30)	120.5(2)
C(3)-C(2)-C(1)	123.1(2)	C(31)-C(30)-C(29)	120.2(2)
C(2)-C(3)-C(4)	120.8(2)	C(30)-C(31)-C(32)	120.0(2)

C(31)-C(32)-C(33)	120.1(2)	C(43)-C(42)-C(41)	120.2(2)
C(32)-C(33)-C(28)	121.1(2)	C(42)-C(43)-C(44)	119.7(2)
C(39)-C(34)-C(35)	118.6(2)	C(43)-C(44)-C(45)	120.1(2)
C(39)-C(34)-P(3)	118.88(18)	C(40)-C(45)-C(44)	120.9(2)
C(35)-C(34)-P(3)	122.44(18)	N(1)-C(46)-C(51)	120.1(2)
C(36)-C(35)-C(34)	119.9(2)	N(1)-C(46)-C(47)	123.6(2)
C(37)-C(36)-C(35)	120.8(2)	C(51)-C(46)-C(47)	116.3(2)
C(36)-C(37)-C(38)	119.9(2)	C(48)-C(47)-C(46)	121.0(3)
C(39)-C(38)-C(37)	120.1(2)	C(47)-C(48)-C(49)	122.1(2)
C(38)-C(39)-C(34)	120.7(2)	C(50)-C(49)-C(48)	116.6(2)
C(45)-C(40)-C(41)	118.3(2)	C(50)-C(49)-C(52)	120.5(3)
C(45)-C(40)-P(3)	123.61(18)	C(48)-C(49)-C(52)	122.9(3)
C(41)-C(40)-P(3)	118.08(18)	C(51)-C(50)-C(49)	122.0(3)
C(42)-C(41)-C(40)	120.8(2)	C(50)-C(51)-C(46)	122.0(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for [$PhBP_3$]Fe(N(H)-*p*-tolyl) (**2**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe(1)	19(1)	21(1)	20(1)	-5(1)	-3(1)	-1(1)
N(1)	29(1)	27(1)	21(1)	-8(1)	4(1)	-11(1)
P(1)	21(1)	18(1)	19(1)	-3(1)	-3(1)	-1(1)
P(2)	21(1)	17(1)	18(1)	-4(1)	-5(1)	-1(1)
P(3)	18(1)	20(1)	23(1)	-6(1)	-7(1)	2(1)
B(1)	18(2)	20(2)	18(1)	-5(1)	-4(1)	1(1)
C(1)	21(1)	15(1)	17(1)	0(1)	-4(1)	1(1)
C(2)	20(2)	52(2)	29(1)	-16(1)	0(1)	-15(1)
C(3)	33(2)	66(2)	24(1)	-23(1)	3(1)	-20(2)
C(4)	25(2)	35(2)	21(1)	-7(1)	3(1)	-3(1)
C(5)	17(1)	38(2)	27(1)	-8(1)	-7(1)	1(1)
C(6)	24(1)	30(2)	19(1)	-9(1)	-9(1)	5(1)
C(7)	21(1)	22(1)	14(1)	-5(1)	-3(1)	0(1)
C(8)	16(1)	18(1)	19(1)	-3(1)	-4(1)	2(1)
C(9)	22(1)	19(1)	21(1)	-3(1)	-5(1)	-2(1)
C(10)	31(2)	18(1)	18(1)	-3(1)	2(1)	-6(1)
C(11)	54(2)	33(2)	28(2)	6(1)	-13(1)	-17(2)
C(12)	72(2)	52(2)	28(2)	-3(2)	-13(2)	-34(2)
C(13)	83(3)	28(2)	32(2)	-10(1)	8(2)	-22(2)
C(14)	55(2)	25(2)	68(2)	-3(2)	2(2)	-1(2)
C(15)	36(2)	22(2)	61(2)	-5(1)	-5(2)	-2(1)
C(16)	26(2)	13(1)	19(1)	-1(1)	-9(1)	2(1)
C(17)	27(2)	24(2)	26(1)	-4(1)	-4(1)	1(1)
C(18)	49(2)	29(2)	19(1)	-2(1)	-9(1)	2(1)
C(19)	41(2)	30(2)	31(2)	-1(1)	-23(1)	4(1)
C(20)	26(2)	36(2)	38(2)	-4(1)	-13(1)	6(1)
C(21)	29(2)	26(2)	21(1)	-3(1)	-5(1)	2(1)
C(22)	21(1)	18(1)	16(1)	-7(1)	-4(1)	2(1)
C(23)	25(2)	24(2)	32(1)	-6(1)	-4(1)	-1(1)
C(24)	41(2)	23(2)	36(2)	-5(1)	2(1)	-6(1)
C(25)	62(2)	19(2)	19(1)	-3(1)	-8(1)	8(2)

C(26)	37(2)	32(2)	32(2)	-12(1)	-18(1)	13(1)
C(27)	27(2)	29(2)	26(1)	-11(1)	-9(1)	1(1)
C(28)	22(1)	15(1)	20(1)	-1(1)	-6(1)	-4(1)
C(29)	24(1)	22(2)	23(1)	-7(1)	-3(1)	0(1)
C(30)	25(2)	27(2)	30(1)	-2(1)	-13(1)	-2(1)
C(31)	40(2)	26(2)	22(1)	-2(1)	-13(1)	-7(1)
C(32)	39(2)	38(2)	21(1)	-10(1)	-4(1)	5(1)
C(33)	26(2)	39(2)	22(1)	-7(1)	-7(1)	4(1)
C(34)	19(1)	19(1)	26(1)	-10(1)	-11(1)	4(1)
C(35)	25(2)	34(2)	22(1)	-11(1)	-7(1)	4(1)
C(36)	37(2)	29(2)	27(1)	-4(1)	-15(1)	6(1)
C(37)	31(2)	32(2)	40(2)	-13(1)	-18(1)	12(1)
C(38)	19(1)	35(2)	36(2)	-17(1)	-7(1)	4(1)
C(39)	21(1)	24(2)	28(1)	-9(1)	-10(1)	-1(1)
C(40)	19(1)	19(1)	27(1)	-6(1)	-11(1)	4(1)
C(41)	26(2)	32(2)	30(1)	-12(1)	-1(1)	1(1)
C(42)	22(2)	33(2)	45(2)	-11(1)	-3(1)	-7(1)
C(43)	30(2)	29(2)	42(2)	-18(1)	-12(1)	-2(1)
C(44)	32(2)	32(2)	32(2)	-16(1)	-6(1)	1(1)
C(45)	21(1)	23(2)	30(1)	-4(1)	-6(1)	0(1)
C(46)	16(1)	27(2)	30(1)	-4(1)	-8(1)	-2(1)
C(47)	36(2)	32(2)	26(1)	-3(1)	-11(1)	2(1)
C(48)	45(2)	51(2)	18(1)	-9(1)	-11(1)	7(2)
C(49)	38(2)	45(2)	33(2)	-20(1)	-16(1)	10(2)
C(50)	29(2)	30(2)	53(2)	-13(1)	-9(1)	-4(1)
C(51)	30(2)	31(2)	33(2)	-5(1)	1(1)	-3(1)
C(52)	59(2)	60(2)	44(2)	-29(2)	-19(2)	13(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [$PhBP_3$]Fe(N(H)-*p*-tolyl) (**2**).

	x	y	z	U(eq)
H(1)	2359	1281	4091	31
H(2)	7152	2074	-603	39
H(3)	8975	1919	-1766	48
H(4)	11190	2246	-1659	33
H(5)	11507	2763	-359	32
H(6)	9673	2926	803	28
H(7A)	7601	1064	1457	23
H(7B)	6182	1101	1133	23
H(8A)	7773	3595	1580	21
H(8B)	7952	2637	2203	21
H(9A)	5559	2873	138	25
H(9B)	5549	3642	751	25
H(11)	3664	208	2187	46
H(12)	2896	-1282	2302	59
H(13)	3968	-2505	3057	59
H(14)	5856	-2270	3639	62
H(15)	6663	-794	3492	49
H(17)	5547	951	4572	31
H(18)	6994	833	5592	39
H(19)	9355	782	5080	39
H(20)	10271	815	3534	39
H(21)	8805	904	2511	30
H(23)	7416	4997	2347	32
H(24)	6982	6537	1851	41
H(25)	4832	7004	1568	40
H(26)	3102	5947	1829	38
H(27)	3518	4413	2374	31
H(29)	8475	2905	3427	27
H(30)	9215	3086	4739	32
H(31)	7763	3732	5870	34

H(32)	5540	4148	5725	39
H(33)	4787	3966	4428	34
H(35)	3550	4147	-8	31
H(36)	1985	5358	-121	36
H(37)	102	5454	1038	39
H(38)	-243	4331	2335	34
H(39)	1301	3116	2468	27
H(41)	1461	1499	1872	35
H(42)	612	347	1290	40
H(43)	1847	-148	-15	38
H(44)	3952	501	-727	37
H(45)	4821	1643	-137	29
H(47)	1334	1322	5716	37
H(48)	407	2241	6776	45
H(50)	1618	4489	4951	43
H(51)	2521	3588	3880	39
H(52A)	312	4717	6358	77
H(52B)	898	4034	7123	77
H(52C)	-603	3893	6966	77

Table 6. Crystal data and structure refinement for [$PhBP_3$]Fe(η^5-cyclohexadienyl) (**3**).

Identification code	sdb35	
Empirical formula	C_{51} H_{48} B Fe P_3	
Formula weight	820.46	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 13.8476(9) Å	α= 90°.
	b = 14.5772(9) Å	β= 90°.
	c = 20.3589(13) Å	γ = 90°.
Volume	4109.6(5) $Å^3$	
Z	4	
Density (calculated)	1.326 Mg/m^3	
Absorption coefficient	0.520 mm^{-1}	
F(000)	1720	
Crystal size	0.067 x 0.17 x 0.22 mm^3	
Theta range for data collection	1.72 to 28.43°.	
Index ranges	-18<=h<=17, -19<=k<=19, -26<=l<=27	
Reflections collected	60994	
Independent reflections	9578 [R(int) = 0.1174]	
Completeness to theta = 28.43°	95.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9578 / 0 / 505	
Goodness-of-fit on F^2	1.130	
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.0629	
R indices (all data)	R1 = 0.0937, wR2 = 0.0688	
Absolute structure parameter	-0.023(14)	
Largest diff. peak and hole	0.478 and -0.597 e.$Å^{-3}$	

Special Refinement Details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

The Flack parameter was included in the full matrix along with all other parameters and refined to a value of 0.00001 with an esd of 0.014, unambiguously indicating that the crystal consists of only one enantiomorph. Consequently, this parameter was not included in the final least squares analysis.

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for [$PhBP_3$]Fe(η^5-cyclohexadienyl) (**3**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Fe	6578(1)	9445(1)	9534(1)	14(1)
P(3)	5389(1)	8379(1)	9564(1)	14(1)
P(2)	5543(1)	10440(1)	10025(1)	14(1)
P(1)	6081(1)	9928(1)	8528(1)	15(1)
C(28)	5443(2)	10468(2)	10929(2)	14(1)
C(11)	5499(3)	8540(2)	7620(2)	18(1)
C(40)	5590(3)	7219(2)	9222(2)	14(1)
C(39)	5679(3)	7484(2)	10774(2)	18(1)
C(16)	6599(3)	10934(2)	8092(2)	15(1)
C(1)	2946(2)	9998(2)	8884(2)	13(1)
C(30)	4755(3)	11208(2)	11883(2)	27(1)
C(10)	6240(2)	9085(2)	7859(2)	15(1)
C(13)	6555(3)	7821(2)	6854(2)	26(1)
C(15)	7156(3)	8986(2)	7570(2)	19(1)
C(35)	4233(2)	8382(2)	10719(2)	17(1)
C(4)	987(2)	10460(2)	8655(2)	23(1)
C(43)	5739(2)	5483(2)	8635(2)	21(1)
C(22)	5883(2)	11655(2)	9898(2)	14(1)
C(32)	5713(2)	9862(2)	12019(2)	22(1)
B	4076(3)	9818(2)	9071(2)	13(1)
C(5)	1692(3)	10756(2)	8237(2)	29(1)
C(36)	4038(3)	8179(2)	11374(2)	21(1)
C(37)	4666(3)	7634(2)	11727(2)	21(1)
C(2)	2199(2)	9691(2)	9291(2)	19(1)
C(8)	4291(2)	10377(2)	9753(1)	15(1)
C(34)	5058(2)	8062(2)	10411(2)	15(1)
C(41)	4991(2)	6499(2)	9411(2)	16(1)
C(27)	6661(3)	12030(2)	10236(2)	20(1)
C(31)	5170(2)	10558(2)	12289(2)	24(1)
C(21)	7090(2)	11639(2)	8412(2)	23(1)
C(33)	5846(2)	9821(2)	11340(2)	15(1)

C(9)	4255(2)	8697(2)	9180(2)	15(1)
C(24)	5688(3)	13119(2)	9354(2)	27(1)
C(44)	6334(2)	6185(2)	8439(2)	21(1)
C(14)	7308(3)	8354(2)	7076(2)	25(1)
C(18)	6666(3)	11846(2)	7100(2)	22(1)
C(7)	4789(2)	10206(2)	8487(1)	15(1)
C(12)	5660(3)	7907(2)	7128(2)	23(1)
C(17)	6393(2)	11062(2)	7425(2)	19(1)
C(25)	6475(3)	13463(2)	9681(2)	28(1)
C(45)	6260(2)	7056(2)	8727(2)	19(1)
C(6)	2651(2)	10522(2)	8344(2)	22(1)
C(42)	5061(2)	5635(2)	9126(2)	19(1)
C(20)	7353(3)	12438(2)	8087(2)	26(1)
C(38)	5480(3)	7280(2)	11427(2)	21(1)
C(23)	5399(3)	12215(2)	9460(2)	23(1)
C(3)	1236(2)	9909(2)	9183(2)	21(1)
C(29)	4888(2)	11169(2)	11212(2)	23(1)
C(26)	6960(3)	12916(2)	10135(2)	26(1)
C(19)	7149(3)	12532(2)	7432(2)	25(1)
C(50)	7595(2)	8394(2)	9665(2)	19(1)
C(47)	7924(2)	10251(2)	9632(2)	20(1)
C(46)	8428(3)	9705(2)	9127(2)	24(1)
C(48)	7645(2)	9849(2)	10224(2)	19(1)
C(51)	7867(2)	8832(2)	9090(2)	20(1)
C(49)	7493(2)	8890(2)	10255(2)	20(1)

Table 8. Bond lengths [Å] and angles [°] for [$PhBP_3$]Fe(η^5-cyclohexadienyl) (**3**).

Fe-C(50)	2.098(3)	C(30)-H(30)	0.9500
Fe-C(49)	2.100(3)	C(10)-C(15)	1.407(4)
Fe-C(48)	2.122(3)	C(13)-C(12)	1.364(5)
Fe-C(51)	2.191(3)	C(13)-C(14)	1.376(5)
Fe-C(47)	2.213(3)	C(13)-H(13)	0.9500
Fe-P(3)	2.2647(9)	C(15)-C(14)	1.381(4)
Fe-P(2)	2.2701(10)	C(15)-H(15)	0.9500
Fe-P(1)	2.2730(10)	C(35)-C(34)	1.385(4)
P(3)-C(9)	1.814(3)	C(35)-C(36)	1.391(4)
P(3)-C(34)	1.843(3)	C(35)-H(35)	0.9500
P(3)-C(40)	1.850(3)	C(4)-C(5)	1.366(4)
P(2)-C(8)	1.823(3)	C(4)-C(3)	1.384(4)
P(2)-C(28)	1.847(3)	C(4)-H(4)	0.9500
P(2)-C(22)	1.850(3)	C(43)-C(44)	1.373(4)
P(1)-C(7)	1.836(3)	C(43)-C(42)	1.390(4)
P(1)-C(10)	1.847(3)	C(43)-H(43)	0.9500
P(1)-C(16)	1.860(3)	C(22)-C(23)	1.382(4)
C(28)-C(33)	1.377(4)	C(22)-C(27)	1.390(4)
C(28)-C(29)	1.403(4)	C(32)-C(31)	1.376(4)
C(11)-C(12)	1.381(4)	C(32)-C(33)	1.397(4)
C(11)-C(10)	1.386(4)	C(32)-H(32)	0.9500
C(11)-H(11)	0.9500	B-C(8)	1.638(4)
C(40)-C(45)	1.390(4)	B-C(7)	1.644(4)
C(40)-C(41)	1.392(4)	B-C(9)	1.669(4)
C(39)-C(38)	1.390(4)	C(5)-C(6)	1.388(4)
C(39)-C(34)	1.412(4)	C(5)-H(5)	0.9500
C(39)-H(39)	0.9500	C(36)-C(37)	1.380(4)
C(16)-C(21)	1.395(4)	C(36)-H(36)	0.9500
C(16)-C(17)	1.399(4)	C(37)-C(38)	1.382(5)
C(1)-C(2)	1.398(4)	C(37)-H(37)	0.9500
C(1)-C(6)	1.399(4)	C(2)-C(3)	1.388(4)
C(1)-B	1.632(5)	C(2)-H(2)	0.9500
C(30)-C(29)	1.379(4)	C(8)-H(8A)	0.9900
C(30)-C(31)	1.382(4)	C(8)-H(8B)	0.9900

C(41)-C(42)	1.390(4)	C(50)-C(51)	1.385(4)
C(41)-H(41)	0.9500	C(50)-C(49)	1.410(4)
C(27)-C(26)	1.373(4)	C(50)-H(50)	0.9500
C(27)-H(27)	0.9500	C(47)-C(48)	1.394(4)
C(31)-H(31)	0.9500	C(47)-C(46)	1.477(4)
C(21)-C(20)	1.388(4)	C(47)-H(47)	0.9500
C(21)-H(21)	0.9500	C(46)-C(51)	1.493(4)
C(33)-H(33)	0.9500	C(46)-H(46A)	0.9900
C(9)-H(9A)	0.9900	C(46)-H(46B)	0.9900
C(9)-H(9B)	0.9900	C(48)-C(49)	1.415(4)
C(24)-C(25)	1.372(4)	C(48)-H(48)	0.9500
C(24)-C(23)	1.395(4)	C(51)-H(51)	0.9500
C(24)-H(24)	0.9500	C(49)-H(49)	0.9500
C(44)-C(45)	1.403(4)		
C(44)-H(44)	0.9500	C(50)-Fe-C(49)	39.25(12)
C(14)-H(14)	0.9500	C(50)-Fe-C(48)	69.64(12)
C(18)-C(17)	1.375(4)	C(49)-Fe-C(48)	39.16(11)
C(18)-C(19)	1.380(4)	C(50)-Fe-C(51)	37.60(12)
C(18)-H(18)	0.9500	C(49)-Fe-C(51)	68.88(13)
C(7)-H(7A)	0.9900	C(48)-Fe-C(51)	79.59(13)
C(7)-H(7B)	0.9900	C(50)-Fe-C(47)	79.12(12)
C(12)-H(12)	0.9500	C(49)-Fe-C(47)	68.46(12)
C(17)-H(17)	0.9500	C(48)-Fe-C(47)	37.43(11)
C(25)-C(26)	1.394(4)	C(51)-Fe-C(47)	64.39(12)
C(25)-H(25)	0.9500	C(50)-Fe-P(3)	89.05(9)
C(45)-H(45)	0.9500	C(49)-Fe-P(3)	99.00(9)
C(6)-H(6)	0.9500	C(48)-Fe-P(3)	132.81(9)
C(42)-H(42)	0.9500	C(51)-Fe-P(3)	108.86(9)
C(20)-C(19)	1.371(4)	C(47)-Fe-P(3)	167.04(9)
C(20)-H(20)	0.9500	C(50)-Fe-P(2)	146.61(10)
C(38)-H(38)	0.9500	C(49)-Fe-P(2)	108.67(10)
C(23)-H(23)	0.9500	C(48)-Fe-P(2)	88.34(9)
C(3)-H(3)	0.9500	C(51)-Fe-P(2)	162.95(9)
C(29)-H(29)	0.9500	C(47)-Fe-P(2)	98.77(9)
C(26)-H(26)	0.9500	P(3)-Fe-P(2)	88.17(3)
C(19)-H(19)	0.9500	C(50)-Fe-P(1)	122.92(10)

C(49)-Fe-P(1)	158.65(10)	C(21)-C(16)-C(17)	117.1(3)
C(48)-Fe-P(1)	136.16(9)	C(21)-C(16)-P(1)	123.1(2)
C(51)-Fe-P(1)	90.06(9)	C(17)-C(16)-P(1)	119.3(2)
C(47)-Fe-P(1)	99.91(9)	C(2)-C(1)-C(6)	115.1(3)
P(3)-Fe-P(1)	90.92(4)	C(2)-C(1)-B	121.3(3)
P(2)-Fe-P(1)	90.40(3)	C(6)-C(1)-B	123.4(3)
C(9)-P(3)-C(34)	104.59(15)	C(29)-C(30)-C(31)	120.5(3)
C(9)-P(3)-C(40)	101.64(14)	C(29)-C(30)-H(30)	119.7
C(34)-P(3)-C(40)	99.22(13)	C(31)-C(30)-H(30)	119.7
C(9)-P(3)-Fe	116.28(10)	C(11)-C(10)-C(15)	117.5(3)
C(34)-P(3)-Fe	112.17(10)	C(11)-C(10)-P(1)	123.5(3)
C(40)-P(3)-Fe	120.52(12)	C(15)-C(10)-P(1)	119.0(2)
C(8)-P(2)-C(28)	103.37(15)	C(12)-C(13)-C(14)	120.1(3)
C(8)-P(2)-C(22)	104.38(14)	C(12)-C(13)-H(13)	119.9
C(28)-P(2)-C(22)	97.91(15)	C(14)-C(13)-H(13)	119.9
C(8)-P(2)-Fe	115.78(10)	C(14)-C(15)-C(10)	120.7(3)
C(28)-P(2)-Fe	119.97(11)	C(14)-C(15)-H(15)	119.7
C(22)-P(2)-Fe	112.96(11)	C(10)-C(15)-H(15)	119.7
C(7)-P(1)-C(10)	103.26(14)	C(34)-C(35)-C(36)	121.5(3)
C(7)-P(1)-C(16)	100.41(14)	C(34)-C(35)-H(35)	119.3
C(10)-P(1)-C(16)	97.25(14)	C(36)-C(35)-H(35)	119.3
C(7)-P(1)-Fe	113.87(10)	C(5)-C(4)-C(3)	119.2(3)
C(10)-P(1)-Fe	114.98(10)	C(5)-C(4)-H(4)	120.4
C(16)-P(1)-Fe	123.91(11)	C(3)-C(4)-H(4)	120.4
C(33)-C(28)-C(29)	118.1(3)	C(44)-C(43)-C(42)	119.7(3)
C(33)-C(28)-P(2)	124.0(2)	C(44)-C(43)-H(43)	120.1
C(29)-C(28)-P(2)	117.8(2)	C(42)-C(43)-H(43)	120.1
C(12)-C(11)-C(10)	121.2(3)	C(23)-C(22)-C(27)	117.5(3)
C(12)-C(11)-H(11)	119.4	C(23)-C(22)-P(2)	122.1(2)
C(10)-C(11)-H(11)	119.4	C(27)-C(22)-P(2)	120.3(2)
C(45)-C(40)-C(41)	118.0(3)	C(31)-C(32)-C(33)	119.9(3)
C(45)-C(40)-P(3)	122.0(2)	C(31)-C(32)-H(32)	120.1
C(41)-C(40)-P(3)	119.7(2)	C(33)-C(32)-H(32)	120.1
C(38)-C(39)-C(34)	120.4(3)	C(1)-B-C(8)	107.0(3)
C(38)-C(39)-H(39)	119.8	C(1)-B-C(7)	110.6(2)
C(34)-C(39)-H(39)	119.8	C(8)-B-C(7)	109.5(3)

C(1)-B-C(9)	109.3(3)	C(28)-C(33)-C(32)	121.2(3)
C(8)-B-C(9)	110.3(3)	C(28)-C(33)-H(33)	119.4
C(7)-B-C(9)	110.1(3)	C(32)-C(33)-H(33)	119.4
C(4)-C(5)-C(6)	120.6(3)	B-C(9)-P(3)	115.8(2)
C(4)-C(5)-H(5)	119.7	B-C(9)-H(9A)	108.3
C(6)-C(5)-H(5)	119.7	P(3)-C(9)-H(9A)	108.3
C(37)-C(36)-C(35)	120.0(3)	B-C(9)-H(9B)	108.3
C(37)-C(36)-H(36)	120.0	P(3)-C(9)-H(9B)	108.3
C(35)-C(36)-H(36)	120.0	H(9A)-C(9)-H(9B)	107.4
C(36)-C(37)-C(38)	119.8(3)	C(25)-C(24)-C(23)	119.9(3)
C(36)-C(37)-H(37)	120.1	C(25)-C(24)-H(24)	120.1
C(38)-C(37)-H(37)	120.1	C(23)-C(24)-H(24)	120.1
C(3)-C(2)-C(1)	122.9(3)	C(43)-C(44)-C(45)	120.6(3)
C(3)-C(2)-H(2)	118.5	C(43)-C(44)-H(44)	119.7
C(1)-C(2)-H(2)	118.5	C(45)-C(44)-H(44)	119.7
B-C(8)-P(2)	117.0(2)	C(13)-C(14)-C(15)	120.1(4)
B-C(8)-H(8A)	108.0	C(13)-C(14)-H(14)	120.0
P(2)-C(8)-H(8A)	108.0	C(15)-C(14)-H(14)	120.0
B-C(8)-H(8B)	108.0	C(17)-C(18)-C(19)	120.0(3)
P(2)-C(8)-H(8B)	108.0	C(17)-C(18)-H(18)	120.0
H(8A)-C(8)-H(8B)	107.3	C(19)-C(18)-H(18)	120.0
C(35)-C(34)-C(39)	117.8(3)	B-C(7)-P(1)	118.4(2)
C(35)-C(34)-P(3)	123.0(3)	B-C(7)-H(7A)	107.7
C(39)-C(34)-P(3)	119.2(3)	P(1)-C(7)-H(7A)	107.7
C(42)-C(41)-C(40)	121.7(3)	B-C(7)-H(7B)	107.7
C(42)-C(41)-H(41)	119.1	P(1)-C(7)-H(7B)	107.7
C(40)-C(41)-H(41)	119.1	H(7A)-C(7)-H(7B)	107.1
C(26)-C(27)-C(22)	122.0(3)	C(13)-C(12)-C(11)	120.3(3)
C(26)-C(27)-H(27)	119.0	C(13)-C(12)-H(12)	119.8
C(22)-C(27)-H(27)	119.0	C(11)-C(12)-H(12)	119.8
C(32)-C(31)-C(30)	119.6(3)	C(18)-C(17)-C(16)	121.5(3)
C(32)-C(31)-H(31)	120.2	C(18)-C(17)-H(17)	119.3
C(30)-C(31)-H(31)	120.2	C(16)-C(17)-H(17)	119.3
C(20)-C(21)-C(16)	121.6(3)	C(24)-C(25)-C(26)	119.7(3)
C(20)-C(21)-H(21)	119.2	C(24)-C(25)-H(25)	120.1
C(16)-C(21)-H(21)	119.2	C(26)-C(25)-H(25)	120.1

C(40)-C(45)-C(44)	120.5(3)	C(51)-C(50)-H(50)	119.7
C(40)-C(45)-H(45)	119.8	C(49)-C(50)-H(50)	119.7
C(44)-C(45)-H(45)	119.8	Fe-C(50)-H(50)	127.0
C(5)-C(6)-C(1)	122.4(3)	C(48)-C(47)-C(46)	120.5(3)
C(5)-C(6)-H(6)	118.8	C(48)-C(47)-Fe	67.74(18)
C(1)-C(6)-H(6)	118.8	C(46)-C(47)-Fe	92.8(2)
C(43)-C(42)-C(41)	119.4(3)	C(48)-C(47)-H(47)	119.8
C(43)-C(42)-H(42)	120.3	C(46)-C(47)-H(47)	119.8
C(41)-C(42)-H(42)	120.3	Fe-C(47)-H(47)	109.4
C(19)-C(20)-C(21)	119.6(3)	C(47)-C(46)-C(51)	104.4(3)
C(19)-C(20)-H(20)	120.2	C(47)-C(46)-H(46A)	110.9
C(21)-C(20)-H(20)	120.2	C(51)-C(46)-H(46A)	110.9
C(37)-C(38)-C(39)	120.4(3)	C(47)-C(46)-H(46B)	110.9
C(37)-C(38)-H(38)	119.8	C(51)-C(46)-H(46B)	110.9
C(39)-C(38)-H(38)	119.8	H(46A)-C(46)-H(46B)	108.9
C(22)-C(23)-C(24)	121.3(3)	C(47)-C(48)-C(49)	119.6(3)
C(22)-C(23)-H(23)	119.4	C(47)-C(48)-Fe	74.83(19)
C(24)-C(23)-H(23)	119.4	C(49)-C(48)-Fe	69.59(19)
C(4)-C(3)-C(2)	119.7(3)	C(47)-C(48)-H(48)	120.2
C(4)-C(3)-H(3)	120.2	C(49)-C(48)-H(48)	120.2
C(2)-C(3)-H(3)	120.2	Fe-C(48)-H(48)	127.4
C(30)-C(29)-C(28)	120.6(3)	C(50)-C(51)-C(46)	119.5(3)
C(30)-C(29)-H(29)	119.7	C(50)-C(51)-Fe	67.54(19)
C(28)-C(29)-H(29)	119.7	C(46)-C(51)-Fe	93.2(2)
C(27)-C(26)-C(25)	119.5(3)	C(50)-C(51)-H(51)	120.2
C(27)-C(26)-H(26)	120.3	C(46)-C(51)-H(51)	120.2
C(25)-C(26)-H(26)	120.3	Fe-C(51)-H(51)	108.9
C(20)-C(19)-C(18)	120.3(3)	C(50)-C(49)-C(48)	117.1(3)
C(20)-C(19)-H(19)	119.8	C(50)-C(49)-Fe	70.28(19)
C(18)-C(19)-H(19)	119.8	C(48)-C(49)-Fe	71.25(19)
C(51)-C(50)-C(49)	120.6(3)	C(50)-C(49)-H(49)	121.5
C(51)-C(50)-Fe	74.9(2)	C(48)-C(49)-H(49)	121.5
C(49)-C(50)-Fe	70.47(18)	Fe-C(49)-H(49)	129.1

Symmetry transformations used to generate equivalent atoms:

Table 9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $[PhBP_3]Fe(\eta^5$-cyclohexadienyl) (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Fe	14(1)	14(1)	15(1)	0(1)	-1(1)	0(1)
P(3)	16(1)	12(1)	13(1)	0(1)	2(1)	1(1)
P(2)	17(1)	14(1)	12(1)	0(1)	-1(1)	-1(1)
P(1)	15(1)	14(1)	14(1)	0(1)	1(1)	-1(1)
C(28)	12(2)	16(2)	15(2)	-2(2)	-3(2)	0(2)
C(11)	20(2)	18(2)	15(2)	-1(2)	0(2)	1(2)
C(40)	17(2)	14(2)	10(2)	2(1)	-2(2)	-1(2)
C(39)	15(2)	20(2)	20(2)	-1(2)	0(2)	-2(2)
C(16)	12(2)	16(2)	17(2)	1(1)	-2(2)	3(2)
C(1)	18(2)	9(2)	11(2)	-3(1)	2(2)	3(2)
C(30)	31(3)	35(2)	16(2)	-10(2)	1(2)	5(2)
C(10)	20(2)	12(2)	14(2)	4(1)	-1(2)	-2(2)
C(13)	37(3)	20(2)	20(2)	-8(2)	5(2)	2(2)
C(15)	22(2)	18(2)	16(2)	-2(2)	-1(2)	-1(2)
C(35)	16(2)	18(2)	17(2)	2(2)	-2(2)	-5(2)
C(4)	12(2)	32(2)	27(2)	-3(2)	-6(2)	3(2)
C(43)	28(2)	11(2)	23(2)	0(2)	-6(2)	4(2)
C(22)	16(2)	15(2)	12(2)	-4(1)	1(2)	-3(2)
C(32)	31(2)	23(2)	12(2)	5(2)	-11(2)	-8(2)
B	14(2)	14(2)	12(2)	1(2)	1(2)	3(2)
C(5)	28(3)	35(2)	23(2)	11(2)	-4(2)	5(2)
C(36)	21(2)	21(2)	21(2)	-3(2)	5(2)	-7(2)
C(37)	27(3)	20(2)	16(2)	3(2)	-5(2)	-4(2)
C(2)	17(2)	18(2)	21(2)	7(2)	-5(2)	-1(2)
C(8)	17(2)	14(2)	14(2)	3(1)	-2(1)	3(2)
C(34)	15(2)	16(2)	13(2)	-3(2)	-4(2)	-4(1)
C(41)	12(2)	16(2)	20(2)	0(2)	2(2)	4(2)
C(27)	23(2)	18(2)	19(2)	4(1)	-4(2)	-2(2)
C(31)	25(2)	35(2)	10(2)	-4(2)	1(2)	-6(2)
C(21)	27(2)	20(2)	21(2)	5(2)	-5(2)	0(2)
C(33)	13(2)	13(2)	21(2)	-3(1)	-5(2)	-2(2)

C(9)	11(2)	18(2)	17(2)	-1(1)	1(2)	-4(2)
C(24)	43(3)	14(2)	22(2)	2(2)	-7(2)	2(2)
C(44)	27(3)	20(2)	17(2)	2(2)	7(2)	3(2)
C(14)	27(3)	24(2)	25(2)	-2(2)	6(2)	8(2)
C(18)	26(2)	23(2)	17(2)	2(2)	4(2)	5(2)
C(7)	17(2)	10(2)	18(2)	-1(1)	-2(2)	-1(1)
C(12)	29(3)	24(2)	16(2)	-7(2)	-2(2)	-4(2)
C(17)	17(2)	19(2)	20(2)	-2(2)	1(2)	2(2)
C(25)	46(3)	17(2)	22(2)	1(2)	2(2)	-8(2)
C(45)	22(2)	20(2)	16(2)	4(2)	-1(2)	-4(2)
C(6)	15(2)	34(2)	18(2)	6(2)	4(2)	2(2)
C(42)	22(2)	10(2)	24(2)	1(2)	3(2)	-8(2)
C(20)	21(2)	29(2)	30(3)	-4(2)	2(2)	-8(2)
C(38)	22(2)	26(2)	15(2)	6(2)	-5(2)	-2(2)
C(23)	32(2)	16(2)	20(2)	3(2)	-6(2)	-1(2)
C(3)	10(2)	23(2)	30(2)	3(2)	2(2)	-5(2)
C(29)	26(2)	29(2)	13(2)	4(2)	-8(2)	5(2)
C(26)	29(3)	21(2)	28(2)	-5(2)	2(2)	-8(2)
C(19)	23(3)	18(2)	35(3)	7(2)	5(2)	3(2)
C(50)	16(2)	18(2)	24(2)	-1(2)	-2(2)	2(2)
C(47)	16(2)	19(2)	24(2)	0(2)	-1(2)	1(2)
C(46)	13(2)	27(2)	31(2)	2(2)	-2(2)	-5(2)
C(48)	12(2)	26(2)	20(2)	-3(2)	-6(2)	-2(2)
C(51)	18(2)	21(2)	21(2)	1(2)	-4(2)	4(2)
C(49)	19(2)	20(2)	20(2)	3(2)	-4(2)	-2(2)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for [$PhBP_3$]Fe(η^5-cyclohexadienyl) (**3**).

	x	y	z	U(eq)
H(11)	4868	8604	7798	21
H(39)	6237	7232	10570	22
H(30)	4375	11685	12068	33
H(13)	6658	7394	6509	31
H(15)	7677	9358	7717	22
H(35)	3789	8748	10479	20
H(4)	333	10631	8586	28
H(43)	5791	4896	8435	25
H(32)	5996	9410	12295	26
H(5)	1525	11125	7870	35
H(36)	3473	8415	11577	25
H(37)	4539	7503	12176	26
H(2)	2358	9317	9657	22
H(8A)	3909	10086	10108	18
H(8B)	4047	11011	9700	18
H(41)	4522	6601	9744	19
H(27)	6996	11661	10545	24
H(31)	5081	10591	12751	28
H(21)	7248	11571	8864	27
H(33)	6221	9339	11157	19
H(9A)	4217	8391	8747	19
H(9B)	3721	8454	9453	19
H(24)	5340	13497	9055	32
H(44)	6799	6080	8104	26
H(14)	7932	8286	6889	30
H(18)	6522	11916	6646	26
H(7A)	4727	10882	8478	18
H(7B)	4539	9974	8063	18
H(12)	5146	7529	6980	28
H(17)	6056	10596	7193	22

H(25)	6688	14072	9598	34
H(45)	6671	7538	8584	23
H(6)	3125	10725	8039	27
H(42)	4648	5152	9266	22
H(20)	7673	12917	8318	32
H(38)	5906	6896	11668	25
H(23)	4859	11979	9227	27
H(3)	751	9680	9469	25
H(29)	4602	11623	10939	27
H(26)	7494	13155	10373	31
H(19)	7341	13071	7205	30
H(50)	7475	7752	9661	23
H(47)	7789	10881	9554	23
H(46A)	9105	9585	9257	29
H(46B)	8424	10026	8698	29
H(48)	7557	10217	10604	23
H(51)	7697	8579	8676	24
H(49)	7331	8594	10655	24